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<b>(21) International Application Number:</b> PCT/GB98/02483 <b>(22) International Filing Date:</b> 19 August 1998 (19.08.98) <b>(30) Priority Data:</b> 9718059.0 28 August 1997 (28.08.97) GB <b>(71) Applicant (for all designated States except US):</b> JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ANDERSEN, Paul, Joseph [US/US]; 355 Brighton Road, Norristown, PA 19401 (US). BALLINGER, Todd, Howard [US/US]; 911 Jode Road, Audubon, PA 19403 (US). LAFYATIS, David, Scott [US/US]; 333 Lancaster Avenue #709, Frazer, PA 19355 (US). RAJARAM, Raj, Rao [MU/GB]; 34 Buckland Avenue, Slough SL3 7PH (GB). WALKER, Andrew, Peter [GB/GB]; 83 St. Nicholas Road, Wallingford OX10 8HY (GB). <b>(74) Agent:</b> WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVEMENTS RELATING TO CATALYSTS  <b>(57) Abstract</b>  Exhaust gas catalysts are poisoned by sulphur species in the fuel, but if mounted under-floor do not reach a temperature at which sulphur may be removed. Periodic oxidation of CO and/or hydrocarbons on the catalyst by the addition of supplementary air can raise the temperature of the catalyst to at least 550 °C, preferably higher, and thus maintain desired catalytic activity.		

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## IMPROVEMENTS RELATING TO CATALYSTS

This invention concerns improvements relating to catalysts, more especially it concerns improvements in automobile emission catalysts.

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The use of such catalysts, also known as catalytic convertors, is very well established in the automobile industry in view of the exhaust gas emission regulations which are in force in most countries. The most common catalysts use a platinum group metal ("PGM") especially one or more of Pt, Pd and Rh, carried on an oxidic high surface area washcoat which is one or more of  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{ZrO}_2$  including mixed oxides thereof or the like. The support for the catalyst is generally a low pressure-drop flow-through honeycomb manufactured from an extruded ceramic, *eg* cordierite, or from a metal honeycomb.

Gasoline contains varying amounts of sulphur depending upon its origins and the amount and type of refining it has been subjected to. Sulphur is a well-known poison of catalyst activity in such catalysts. We believe that the deactivating effect of sulphur may be due to adsorption on either the precious metal or on the support. We have found that sulphur may be removed by increasing the temperature of the catalyst, but that under lean operating conditions, that is when the overall composition of the exhaust gases leaving the engine is oxidising, the temperature required for sulphur removal is higher than under rich conditions. Indeed, we have found that for certain catalysts, the minimum temperature for sulphur removal is  $625^\circ\text{C}$  under lean conditions. This temperature is higher than the catalyst would normally be exposed to in its usual under-floor position mounted on the automobile.

EP 580389 (Toyota) discloses the removal of  $\text{SO}_x$  from a  $\text{NO}_x$  absorbent-type catalyst which is used to treat the exhaust gases from a lean-burn gasoline internal combustion engine, by decreasing the oxygen concentration in the exhaust gases, thus making them rich. That is,  $\text{SO}_x$  is being removed from the  $\text{NO}_x$  absorbent by chemical means. JP 4161251 (Mitsubishi) teaches the removal of  $\text{SO}_x$  from a catalyst for a lean burn internal combustion engine such as a diesel engine, by heating the catalyst to  $450\text{--}800^\circ\text{C}$ . It is plain from the drawings that significant heating is required ( $600^\circ\text{C}$  for 1 hour) in order

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approximately the S-free conversion. Heating at 500°C for 2 hours did not give such good results. Most diesel fuels have a much higher S content than gasolines.

5 The present invention provides a system comprising a gasoline-fuelled internal combustion engine, a three-way catalyst mounted under-floor and arranged to continuously have exhaust gas passed therethrough, and an engine management system, said system being so designed and constructed that during at least one portion of every operation of the engine, the engine management system initiates an operating condition which raises the catalyst temperature to at least 550°C, preferably at least 600°C, more preferably at least 625°C,  
10 whereby sulphur poisoning of the catalyst is reduced.

The invention also provides a method of reducing sulphur poisoning of a three-way catalyst, which method comprises intermittently raising the temperature of the catalyst to at least 550°C, preferably at least 600°C, more preferably at least 625°C whilst continuously  
15 passing exhaust gas therethrough, providing said intermittent heating takes place at least once every engine operation.

The internal combustion engine and its associated controls may be desirably designed in a first embodiment to operate essentially under stoichiometric conditions.  
20

A preferred catalyst for use in this first embodiment incorporates palladium and ceria. A more preferred catalyst is one having ambient temperature CO oxidation activity, as described in our prior patent applications WO 96/39576 and EP 0747581.

25 The system of the first embodiment preferably operates by intermittently oxidising CO and/or hydrocarbon by the addition of a secondary air supply just upstream of the catalyst. The engine management system is therefore designed to initiate a condition in which the exhaust gas is enriched with CO and/or hydrocarbon, and secondary air is added. Accordingly, the exotherm from such oxidation raises the catalyst temperature.

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The first embodiment of the present invention may be operated in several different ways. In a first method, especially when using the preferred catalysts, the engine management system provides a very rich cold start. Oxidation of CO and unburnt hydrocarbon species (using a secondary air supply) on the catalyst immediately begins to  
5 raise the catalyst temperature to a temperature at which sulphur removal under lean conditions takes place, that is preferably above 625°C. More preferably, the rich cold start is continued to bring the catalyst to a temperature of 800-850°C or higher, in order to remove virtually all sulphur species from the catalyst.

10 A second method, which may be combined with the first, utilises a periodic enrichment to, for example, an air/fuel ratio of 10-14 for a pre-set time, for example 5-100 seconds, during normal running, combined with secondary air addition. The catalyst will already be at a normal operating temperature of at least 400°C and therefore does not require as much chemical energy to raise its temperature to an effective sulphur-removal  
15 temperature as does the first embodiment which begins at ambient temperature. In such a second method, the period between initiations of the high temperature may be pre-set in the engine management system memory, or may be variable according to operating conditions and/or either the sulphur content of the fuel, eg as sensed, or some form of feed-back of sulphidation of the catalyst.

20 A modification of this second method arises in a preferred design in which the said catalyst is supplemented by another catalyst, preferably in a close-coupled position close to the engine. The close-coupled catalyst is mounted upstream of the secondary air inlet. This offers particular benefits in that during the high temperature phase, NOx reduction on the  
25 main catalyst is less effective (because of the lean condition due to secondary air addition), but the close-coupled catalyst, which is exposed to the enriched engine-out condition, can still provide NOx removal.

A third method involves removal of sulphur under rich conditions, which may be  
30 achieved at a lower catalyst temperature than when the exhaust gas is stoichiometric or lean. The normal operating temperature of the catalyst is still generally below that at which

5 sulphur may be removed. It is therefore again necessary to raise the catalyst temperature which may be done by enrichment, either on start-up or periodically during operation, by adjusting the air-fuel ratio fed to the engine or by supplementary fuel addition into the exhaust gas stream. Supplementary air addition provides the conditions for exothermic oxidation on the catalyst raising its temperature to or above the required level. Once the required temperature has been reached, suitably at least 550°C, preferably at least 650°C, the supplementary air may be terminated or reduced, so that the exhaust gases are rich, that is there is an excess of reducing species.

10 A second embodiment of the present invention utilises instead of, or to supplement, oxidative heating as in the first embodiment, electric resistive heating of the catalyst. This may be effected by directly heating the catalyst or by positioning an electric heating element upstream of the catalyst. Electrically heated catalysts have been proposed to speed light-off of catalysts upon start-up from cold but because of the high power requirements, have not  
15 met with general acceptance. In this embodiment, because it is envisaged that electric heating will be initiated during operation of the engine, when the catalyst is already at its operating temperature, the power required to reach the desired temperature according to the present invention is comparatively low, and since the time for reaching the desired temperature is not so important, the total power required in this embodiment need not  
20 exceed the power that can be provided by the vehicle's on-board generation capacity, *eg* the engine's alternator. An electrically heated catalyst as proposed in the art requires a second battery, with consequential design, engineering and weight costs. We are not aware of any prior proposal which contemplates electric heating of a catalyst in a gasoline-powered vehicle at any point during normal operation of the engine.

25

This second embodiment of the invention is believed to have particular application for lean-burn gasoline engines, especially for gasoline direct injection. For such lean-burn engines, the catalyst desirably comprises a NO<sub>x</sub>-storage component such as baria and/or  
30 calcia.

It will be appreciated that the actual conditions, time periods and other parameters relevant to sulphur removal depend upon the engine and emission system design and general operating conditions, as well as the results desired, and may be determined by conventional optimisation.

The first embodiment of the invention is believed to offer particular advantages with the preferred catalysts mentioned above, and permits the maintenance of low temperature light-off capability.

The invention will now be described by way of example only.

#### 1. Preparation of Pd/CeO<sub>2</sub> Catalyst

Commercially available CeO<sub>2</sub> particles were impregnated using tetraammine palladium hydrogen carbonate solution so that the PGM content was 8%Pd by weight. This was then coated onto a 400 cells *per* square inch (62 cells/cm<sup>2</sup>) monolith at a loading of 3g/in<sup>3</sup> (0.18g/cm<sup>3</sup>).

#### 2. Experimental Evaluation Protocols

In order to test catalysts on a micro reactor, the following evaluation procedures were adopted.

##### Test 1 Protocol

Prior to experiment, the catalyst is heated to 425°C in a stream of argon with 5%O<sub>2</sub>. The catalyst is then cooled to ambient temperature in this stream. Temperature ramp at the catalyst inlet starts at time=0 from ambient temperature, as shown in Figure 1. At time=0, the following species are also fed to the reactor (GHSV=30,000);

500ppm NO  
600ppm C<sub>3</sub>H<sub>6</sub>  
15% CO<sub>2</sub>  
10% H<sub>2</sub>O  
4% CO

Evaluation is performed by measuring the average CO conversion during the first 20 seconds of the experiment (while the catalyst inlet temperature is still below 50°C).

#### 10 Test 2 Protocol

Prior to experiment, the catalyst is heated to 425°C in a stream of argon with 5%O<sub>2</sub>. The catalyst is then cooled to ambient temperature in this stream. Temperature ramp at the catalyst inlet starts at time=0 from ambient temperatures, as shown in Figure 1. At time=0, the following species are also fed to the reactor (GHSV=30,000)

15 15% CO<sub>2</sub>  
4% CO

20 Evaluation is performed by measuring the average CO conversion during the first 20 seconds of the experiment (while the catalyst inlet temperature is still below 50°C).

This test protocol is somewhat less stringent than the Test 1 protocol, because there are fewer inhibiting species present in the feed.

25 For a series of further tests, catalysts were aged by exposure to a variety of gases and conditions. The gas concentrations for tests 1A to 1E are specified in the Table below, the balance being N<sub>2</sub>, under the conditions specified below for the various tests.



Test	C <sub>3</sub> H <sub>6</sub>	NO <sub>x</sub>	SO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	CO
1A	600ppm	500ppm	0ppm	4%	15%	1.5%
1B	600ppm	500ppm	5ppm	4%	15%	1.5%
1C	600ppm	500ppm	5ppm	11%	15%	8.5%
1D	600ppm	500ppm	5ppm	11%	15%	9%/1.5% cycles
1E	600ppm	500ppm	5ppm	11%	15%	9%/1.5% cycles

### 3. Examples 1A, 1B and 1C: Steady-State Ageing Condition

Three identical catalyst samples were aged in a micro-reactor under lean conditions in feeds containing CO, O<sub>2</sub>, CO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, NO at a GHSV of 100,000 and at a catalyst inlet temperature of 350°C for 14 hours. In Example 1A, the feed contained 1.5%CO and 4%O<sub>2</sub>, and the temperature measured in the catalyst bed was 435°C.

In Example 1B, the feed contained 1.5%CO, 4%O<sub>2</sub> and 5ppm SO<sub>2</sub>, and the temperature measured in the catalyst bed was 435°C.

In Example 1C, the feed contained 8.5%CO, 11%O<sub>2</sub> and 5ppm SO<sub>2</sub>, and the temperature measured in the catalyst bed was 860°C.

Table 1 shows the resulting catalyst performance following these steady-state ageing conditions.

**TABLE 1**

Sample (ageing conditions)	%CO Conversion Protocol 1	%CO Conversion Protocol 2
1A (low temperature, no SO <sub>2</sub> )	97%	not tested
1B (low temperature, with SO <sub>2</sub> )	not tested	0%
1C (high temperature, with SO <sub>2</sub> )	86%	not tested

As can be seen from these results, low temperature ageing in the absence of SO<sub>2</sub> (Sample 1A) leaves a catalyst with excellent levels of low temperature CO oxidation activity in the stringent test protocol 1. However, the addition of sulphur to the feed during this low temperature ageing (sample 1B) completely removes all of this low temperature activity. This is caused by sulphur poisoning of the active sites. The deleterious effect of sulphur on the catalyst activity is negated, however, when the ageing is performed at elevated temperature (as in sample 1C). This is because the sulphur does not adsorb onto the catalyst under these conditions.

#### 4. Examples 1D and 1E - Cycled Ageing Condition

The above Example shows that by keeping the catalyst continually hot (>800°C) under normal lean operation the catalyst can maintain its excellent low temperature activity. However, under real driving conditions it may be more practical (*ie* fuel efficient) to expose the catalyst to high temperature conditions only on a periodic basis.

Two more catalysts were aged in the micro reactor under lean conditions in feeds containing CO, O<sub>2</sub>, CO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, NO and 5ppm SO<sub>2</sub> at a GHSV of 100,000 and at a catalyst inlet temperature of 350°C for 14 hours. In both ageings, the oxygen concentration was held at 11%.

In Example D: the catalyst was aged under cyclic conditions with a 300-second period;

100 seconds: 9% CO, bed temperature  $\approx 880^{\circ}\text{C}$ ;

200 seconds: 1.5%CO, bed temperature  $\approx 420^{\circ}\text{C}$ ;

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In Example 1E: the catalyst was aged under cyclic conditions with a 1000-second period;

100 seconds: 9%CO, bed temperature  $\approx 800^{\circ}\text{C}$ ;

900 seconds: 1.5%CO, bed temperature  $\approx 430^{\circ}\text{C}$ .

10

Table 2 shows the evaluation results following these cycled ageing conditions.

**TABLE 2**

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Sample	%CO Conversion Protocol 1	%CO Conversion Protocol 2
1D	71%	91%
1E	38%	62%

20

Table 2 shows that high levels of low temperature CO activity are retained by the catalysts following such a cycled ageing protocol. It is also worth noting that using mass spectrometry,  $\text{SO}_2$  was identified leaving the catalyst during the high temperature portions of these cycles. Thus, such a cycled ageing protocol may be used to deliberately remove sulphur and enhance the activity of such catalysts.

25

**CLAIMS**

1. A system comprising a gasoline-fuelled internal combustion engine, a three-way catalyst mounted under-floor and arranged to continuously have exhaust gas passed therethrough, and an engine management system, so designed and constructed that during at least one portion of every operation of the engine, the engine management system initiates an operating condition which raises the catalyst temperature to at least 550°C, whereby sulphur poisoning of the catalyst is reduced.
2. A system according to claim 1, wherein the three-way catalyst comprises palladium and ceria.
3. A system according to claim 1 or 2, comprising also a supplementary three-way catalyst close-coupled to the engine.
4. A system according to any one of the preceding claims, wherein the engine management system is capable of initiating a condition in which the exhaust gases are enriched with CO and/or hydrocarbon and secondary air is added to the engine exhaust gases upstream of the catalyst, to cause an exotherm by oxidation of said CO and/or hydrocarbon.
5. A system according to claim 4, in which the engine operates substantially under stoichiometric conditions.
6. A system according to any one of the preceding claims, comprising also an electrically heated element.
7. A system according to claim 6, wherein the engine is a lean-burn engine.
8. A system according to claim 7, wherein the engine is a gasoline direct injection engine.

9. A method of reducing sulphur poisoning of a three-way catalyst in the exhaust system of a gasoline-fuelled internal combustion engine, which method comprises intermittently raising the temperature of the catalyst to at least 550°C, whilst continuously passing exhaust gas therethrough, providing said intermittent heating takes place at least once every engine operation.

10. A method according to claim 9, wherein heating is carried out to raise the catalyst temperature to at least 600°C.

11. A method according to claim 9 or 10, wherein heating of the catalyst is effected by intermittently enriching the exhaust gases with CO and/or hydrocarbons, and supplementary air is added to the exhaust gases upstream of catalyst to cause catalytic oxidation of said CO and/or hydrocarbons to cause heating of the catalyst.

12. A method according to claim 11, wherein said intermittent oxidation takes place during cold start when the engine is operated under rich conditions and sufficient air is added to provide lean conditions at the catalyst.

13. A method according to claim 12, wherein oxidation is carried out under conditions and for a time to raise the catalyst temperature to at least 800°C.

14. A method according to claim 11, wherein engine management provides for a periodic enrichment for a pre-set time.

15. A method according to claim 11, wherein enrichment is effected by adjusting the air-fuel ratio fed to the engine or by supplementary fuel addition into the exhaust gas stream, supplementary air is added downstream of the engine and upstream of the catalyst to cause oxidation to raise the catalyst temperature to at least 550°C and subsequently terminating or reducing the supplementary air to expose the catalyst to exhaust gases that are rich.

16. A method according to claim 9 or 10, wherein electric resistance heating is used to directly heat the catalyst or to further heat the exhaust gases.

*Fig. 1.*